Photon Statistics for Single Molecule Non-Linear Spectroscopy

F. Shikerman, E. Barkai

Department of Physics, Bar Ilan University, Ramat-Gan 52900 Israel

We develop the theory of non linear spectroscopy for a single molecule undergoing stochastic dynamics and interacting with a sequence of two laser pulses. We find general expressions for the photon counting statistics and the exact solution to the problem for the Kubo-Anderson process. In the limit of impulsive pulses the information on the photon statistics is contained in the molecule's dipole correlation function. The selective limit, the semi-classical approximation, and the fast modulation limit, exhibit rich general behaviors of this new type of spectroscopy. We show how the design of external fields leads to insights on ultra-fast dynamics of individual molecule's which are different than those found for an ensemble.

Nonlinear optical interaction of a sequence of laser pulses with matter provides a powerful tool for the investigation of dynamics of ensembles of molecules in a wide variety of chemical, physical and biological systems [1]. Recently, van Dijk et al [2] reported of the first experimental study of an ultra-fast pump-probe single molecule system. Unlike the previous approaches to non-linear spectroscopy where only the ensemble average response to the external fields is resolved, the new approach yields direct information on single molecule dynamics, gained through the analysis of photon counting statistics. Although the original experiment [2] was conducted on a molecule undergoing a relatively simple relaxation process, the huge potential of combining nonlinear spectroscopy with single molecule spectroscopy, inspires many unanswered theoretical questions: What are the fundamental physical limitations of the investigation of fast dynamics when spectral selectivity (defined below) is limited? How does the information contained in these experiments differ from the information contained in simpler continuous wave experiments? What is the finger print of coherence in these type of experiments, and precisely how its influence on photon statistics is suppressed due to dephasing processes? Finally, how to design the external control fields so that new information on dynamics of molecules is gained. While the answer to these questions, depends on the particular dynamics of the molecule under investigation, we present a theory based on the Kubo-Anderson model, which yields general insights on the problem.

Consider a sequence of two laser pulses interacting with a single quantum system as a molecule, an atom, or a nano-crystal. The pulses are assumed to be very short compared with the radiative life-time of the emitter, so that the probability of photon emission during a pulse is negligible, hence a pair of pulses yields two photons at most. Repeating the experiment many times one may obtain the probabilities P_0, P_1 and P_2 of emitting $0, 1$ and 2 photons. In this manuscript we investigate the relation between P_0, P_1 and P_2 and the dynamics of the underlying system interacting with the external fields.

In turn this type of photon statistics reveals important information on fast dynamics of molecules in the condensed phase, information which is very difficult to obtain using other theoretical approaches to single molecule spectroscopy [3, 4, 5, 6, 7, 8]. We consider a model of a single molecule undergoing spectral diffusion and interacting with a pump-probe set up and show that depending on characteristics of the stochastic process and laser field parameters, different types of nonlinear spectroscopies emerge. In particular, sensitivity to the phase accumulated by the molecule in the delay period is found and impulsive and selective type of spectroscopies are considered in detail. Spectral diffusion used here as a prototype of the molecule's dynamics, is found in many molecular systems [7, 9, 10, 11], is easy to detect using the spectral trail technique, when the process is slow. Our goal is developing general methods suitable for the detection of a wider range of dynamics.

The treatment begins with a two level molecule interacting with a time dependent laser field according to the optical Bloch equation [1]

$$\dot{\sigma} = \hat{L}(t)\sigma + \hat{\Gamma}\sigma \tag{1}$$

where $\sigma = (\sigma_{\text{ee}}, \sigma_{\text{gg}}, \sigma_{\text{ge}}, \sigma_{\text{eg}})$. As usual σ_{ee} and σ_{gg} are the populations of the excited and ground states, and $\sigma_{\text{ge}}, \sigma_{\text{eg}}$ are the off diagonal matrix elements of the density matrix. The operator

$$\hat{L}(t) = \begin{pmatrix} -\Gamma & 0 & -i\Omega f(t) & i\Omega f(t) \\ 0 & 0 & i\Omega f(t) & -i\Omega f(t) \\ -i\Omega f(t) & i\Omega f(t) & i\omega(t) - \Gamma/2 & 0 \\ i\Omega f(t) & -i\Omega f(t) & 0 & -i\omega(t) - \Gamma/2 \end{pmatrix}, \tag{2}$$

describes the interaction of the molecule with the driving electromagnetic field through $\Omega f(t)$ where Ω is the Rabi frequency, while $\omega(t)$ is the time dependent absorption frequency of the molecule soon to be discussed. Finally the operator $\hat{\Gamma} = \Gamma |g\rangle\langle e|$ describes the transition from the excited state into the ground state, due to spontaneous emission with Γ designating the emission rate.

The spectral diffusion process $\omega(t)$ is modeled using the

Kubo-Anderson approach: $\omega(t) = \omega_0 + \delta w(t)$ where ω_0 is the bare absorption frequency of the molecule, and $\delta w(t)$ is a random function of time [1, 12]. We will assume that this process is stationary, its mean is zero, its correlation function is $\langle \delta w(t_0 + t)\delta w(t_0)\rangle = \nu^2 \psi(t)$ with $\psi(0) = 1$ and $\psi(\infty) = 0$. We will later demonstrate our results using the Kubo-Anderson process [7, 13], where $\omega(t) = \omega_0 + \nu$ or $\omega(t) = \omega_0 - \nu$, with the rate R determining the transitions between the $+$ and $-$ states, which was used to model single molecules in low temperature glasses [9].

The photon statistics is obtained from the solution of Eq. (1) in terms of an iterative expansion in $\hat{\Gamma}$ [6]. This yields $\sigma(t) = \sum_{n=0}^{\infty} \sigma^{(n)}(t)$ where

$$\sigma^{(n)}(t) = \int_0^t d\bar{t}_n ... \int_0^{\bar{t}_2} d\bar{t}_1 \mathcal{G}(t,\bar{t}_n)\hat{\Gamma}...\mathcal{G}(\bar{t}_2,\bar{t}_1)\hat{\Gamma}\mathcal{G}(\bar{t}_1,0)\sigma(0). \tag{3}$$

The Green function $\mathcal{G}(t,t') = \hat{T}\exp\left[\int_{t'}^t \hat{L}(\bar{t})d\bar{t}\right]$ ($\hat{T}$ - the time ordering operator) is the evolution operator in the absence of the spontaneous emission (i.e. without $\hat{\Gamma}$) and therefore $\sigma^{(n)}(t)$ describes the state of the system conditioned by n emission events. The natural basis we shall use is $|e\rangle = (1,0,0,0)$ which means that the molecule is in the electronic excited state, $|g\rangle = (0,1,0,0)$ the ground state, while $|c\rangle = (0,0,1,0)$ and $|c^*\rangle = (0,0,0,1)$ de-

scribe the coherences. Hence, the probability of emission of n photons is $P_n(t) = \langle e|\sigma^{(n)}(t)\rangle + \langle g|\sigma^{(n)}(t)\rangle$, which we calculate below in the limit of long measurement time $t \to \infty$.

In our model two identical pulses: pump and probe interact with the molecule,

$$f(t) = \begin{cases} \cos(\omega_L t) & 0 < t < t_1 \\ 0 & t_1 < t < t_2 \\ \cos[\omega_L(t - t_2)] & t_2 < t < t_3 \\ 0 & t_3 < t \end{cases} \tag{4}$$

where ω_L is the laser frequency, $t_1 = t_3 - t_2 = T$ are pulses duration, and $\Delta = t_2 - t_1$ is the delay between the pulses. Since the Green function can be written as a product of propagators of shorter time intervals: $\mathcal{G}(t,0) = \mathcal{G}(t,t_3)\mathcal{G}(t_3,t_2)\mathcal{G}(t_2,t_1)\mathcal{G}(t_1,0)$, it is possible to treat everyone of them separately by dividing the range of integration over time in Eq. (3), and inserting closure relations in appropriate places. When the laser is turned off the Green functions $\mathcal{G}(t_2,t_1)$ and $\mathcal{G}(t,t_3)$ are nearly trivial, and one may find general expressions for P_n (any n) for a particular realization of the spectral diffusion process. In the limit of two short pulses obeying $\Gamma T \ll 1$ we neglect the processes where photons are emitted during the pulse events, and find

$$P_n = P_n^{\text{Cla}}\left[\omega(t_1), \omega(t_2)\right] + \left\{e^{i\theta\Delta - \Gamma\Delta/2}A_n^{\text{Coh}}\left[\omega(t_1), \omega(t_2)\right] + \text{C.C.}\right\}, \tag{5}$$

here $\theta\Delta = \int_{t_1}^{t_1+\Delta} \omega(t)dt$ is the random phase accumulated in the delay interval. P_n^{Cla} given in Table 1 below, describe the semi-classical paths in the sense that they include only the transitions between the pure excited and ground states, whereas A_n^{Coh} represent the contribution of the coherence to the photon statistics.

n	P_n^{Cla}	A_n^{Coh}
0	$\langle g|\mathcal{G}[\omega(t_2)]|e\rangle\langle e|\mathcal{G}[\omega(t_1)]|g\rangle e^{-\Gamma\Delta} + \langle g|\mathcal{G}[\omega(t_2)]|g\rangle\langle g|\mathcal{G}[\omega(t_1)]|g\rangle$	$\langle g|\mathcal{G}[\omega(t_2)]|c\rangle\langle c|\mathcal{G}[\omega(t_1)]|g\rangle$
1	$\langle g|\mathcal{G}[\omega(t_2)]|g\rangle\langle e|\mathcal{G}[\omega(t_1)]|g\rangle\left(1 - e^{-\Gamma\Delta}\right) + \langle e|\mathcal{G}[\omega(t_2)]|e\rangle\langle e|\mathcal{G}[\omega(t_1)]|g\rangle e^{-\Gamma\Delta}$ $+\langle e|\mathcal{G}[\omega(t_2)]|g\rangle\langle g|\mathcal{G}[\omega(t_1)]|g\rangle$	$\langle e|\mathcal{G}[\omega(t_2)]|c\rangle\langle c|\mathcal{G}[\omega(t_1)]|g\rangle$
2	$\langle e|\mathcal{G}[\omega(t_2)]|g\rangle\langle e|\mathcal{G}[\omega(t_1)]||g\rangle\left(1 - e^{-\Gamma\Delta}\right)$	0

Table 1

In our further calculations we assume that changes in the absorption frequency of the molecule during the pulse events are negligible, namely that the rate of the spectral diffusion process changes R satisfies $RT \ll 1$. As a consequence the random absorption frequency of the molecule at the moment of excitation will be taken as $\omega(t) = \omega(t_1)$ during the first pulse event and $\omega(t) = \omega(t_2)$ during the

second pulse. If this condition is met, the Green functions needed for the calculation of the matrix elements in Table 1 are found within the rotating wave approximation (RWA) [14] $\mathcal{G}[\omega(t_1)] = \mathcal{G}(t_1,0) = \exp\left\{\hat{L}^{\text{RWA}}[\omega(t_1)]T\right\}$

and similarly for $\mathcal{G}\left[\omega(t_2)\right]$,

$$\hat{L}^{\mathrm{RWA}}[\omega(t_1)] = \begin{pmatrix} -\Gamma & 0 & \frac{-i\Omega}{2} & \frac{i\Omega}{2} \\ 0 & 0 & \frac{i\Omega}{2} & \frac{-i\Omega}{2} \\ \frac{-i\Omega}{2} & \frac{i\Omega}{2} & -\frac{\Gamma}{2} - i\delta(t_1) & 0 \\ \frac{i\Omega}{2} & \frac{-i\Omega}{2} & 0 & -\frac{\Gamma}{2} + i\delta(t_1) \end{pmatrix} \tag{6}$$

where $\delta(t_1) = \omega_L - \omega(t_1)$ is the detuning. Otherwise, the pulses yield time average information on the dynamics.

The results in Table 1 describe the possible physical paths of photon emission. For example consider the first term of P_0^{Cla} in Table 1, the molecule starts in the electronic ground state $|g\rangle$, it then evolves with the Green function of the first pulse $\mathcal{G}\left[\omega(t_1)\right]$ without emitting a photon to the excited state $|e\rangle$, it remains in the excited state in the delay period without emitting a photon [with probability $\exp(-\Gamma\Delta)$], and then the second pulse stimulates the molecule from $|e\rangle$ to $|g\rangle$. From Eq. (5) we see that the non-classical terms A_n^{Coh} are important only when $\Gamma\Delta$ is not too large, as expected. Also $A_2^{\mathrm{Coh}} = 0$ in Table 1, since the emission of two photons from two short pulses is possible only when one photon is spontaneously emitted in the time interval between the pulses and the second photon after the second pulse, hence in this case the coherence is lost due to the collapse of the wave function.

When $\Gamma T \to 0$ normalization condition is $P_0 + P_1 + P_2 = 1$ as expected. In this case the spontaneous emission does not contribute during pulse events, and reversibility and symmetry of matrix elements is found: $\langle e|\mathcal{G}[\omega(t_1)]|e\rangle = \langle g|\mathcal{G}[\omega(t_1)]|g\rangle$, $\langle e|\mathcal{G}[\omega(t_1)]|g\rangle =$

$\langle g|\mathcal{G}[\omega(t_1)]|e\rangle$ etc. It is then easy to use Table 1 and show that $P_0^{\mathrm{Cla}}[\omega(t_1), \omega(t_2)] + P_1^{\mathrm{Cla}}[\omega(t_1), \omega(t_2)] + P_2^{\mathrm{Cla}}[\omega(t_1), \omega(t_2)] = 1$, so the classical paths conserve probability, and $A_1^{\mathrm{Coh}} = -A_0^{\mathrm{Coh}}$. These simple relations are valid for any realization of the underlying stochastic process and they are valuable in reducing the number of matrix elements needed for the calculation of the photon statistics for a specific stochastic path.

To obtain the solution of the problem one must take averages of P_n in Eq. (5) over the stochastic process. This requires knowledge of the joint probability density function (PDF) $P[\omega(t_1), \omega(t_2), \theta\Delta]$ of finding the molecule's absorption frequency in the infinitesimal range near $\omega(t_1)$ at t_1, near $\omega(t_2)$ at t_2 with accumulated random phase $\theta\Delta$. Before considering the concrete example of the Kubo Anderson process, we consider different limits allowing us to make a number of conclusions valid for all types of spectral diffusion processes.

Impulsive limit $\nu \ll \Omega$. – Taking the limit $T \to 0$, $\Omega \to \infty$ in the pulse Green function Eq. (6) while ΩT remains finite in such a way that $\nu \ll \Omega$ we define the impulsive limit. The matrix elements of $\mathcal{G}[\omega(t_1)]$ and $\mathcal{G}[\omega(t_2)]$ *become independent of the value of $\omega(t)$ at the moment of the excitation*, provided that the laser detuning is small compared with Ω. Thus instead of the multi variable PDF $P[\omega(t_1), \omega(t_2), \theta\Delta]$ we now have to deal only with the one variable PDF of the phase $\theta\Delta$. As a result the photon statistics shows an interesting relation with linear continuous wave spectroscopy. Using Eqs. (5, 6) and Table 1 we find for stationary processes

$$\lim_{\Omega\to\infty, T\to 0}\langle P_0 \rangle = e^{-\Gamma\Delta}\sin^4\left(\frac{\Omega T}{2}\right) + \cos^4\left(\frac{\Omega T}{2}\right) - \frac{1}{2}e^{-\Gamma\Delta/2}\sin^2(\Omega T)\,\mathrm{Re}\left[\phi(\Delta)e^{i\omega_0\Delta}\right],$$

$$\lim_{\Omega\to\infty, T\to 0}\langle P_1 \rangle = \frac{1}{2}\sin^2\Omega T\left\{1 + e^{-\frac{\Gamma\Delta}{2}}\mathrm{Re}\left[\phi(\Delta)e^{i\omega_0\Delta}\right]\right\}, \qquad \lim_{\Omega\to\infty, T\to 0}\langle P_2 \rangle = \left(1 - e^{-\Gamma\Delta}\right)\sin^4\frac{\Omega T}{2} \tag{7}$$

where

$$\phi(\Delta) = \langle\exp(i\int_0^\Delta \delta\omega(t')\mathrm{d}t')\rangle \tag{8}$$

is the well investigated Kubo-Anderson correlation function whose Fourier transform is the line shape of the molecule according to the Wiener–Khintchine theorem [12]. This type of impulsive limit offers no spectral resolution in the sense that the photon statistics Eq. (7) is sensitive only to the random phase θ accumulated in the time interval between the pulses and not to the temporal state of the molecule at the time of the pulses. From Eq.

(7) we see that for a $\pi/2$ pulse with $\Omega T = \pi/2$ the importance of the coherence terms and hence the correlation function $\phi(\Delta)$, on the photon statistics is the strongest, since the $\pi/2$ pulse excites the off diagonal terms.

Semi-classical approximation. – The influence of coherence on photon statistics in many experimental cases is expected to be difficult to detect. Either due to dephasing effects or simply because of the large value of the optical transition frequency. In these cases a practical approximation is to remove all the coherence terms, and leave only the semi-classical terms P_n^{Cla}. From Table 1 it is easy to see that in this case we must deal

with the two dimensional PDF $P[\omega(t_1), \omega(t_2)]$, instead of $P[\omega(t_1), \omega(t_2), \theta\Delta]$ for the general case. And then

$$\langle P_n \rangle = \langle P_n^{\text{Cla}} \rangle = \int_0^\infty \int_0^\infty P_n^{\text{Cla}} P[\omega(t_1), \omega(t_2)] \mathrm{d}\omega(t_1) \mathrm{d}\omega(t_2). \tag{9}$$

Below we give an explicit example for this case for the two state Kubo-Anderson model.

Exact solution.– Now we obtain the exact solution for the two state Kubo-Anderson Poissonian process, where the absorption frequency of the molecule jumps between a $+$ and $-$ states where $\omega = \omega_0 \pm \nu$. We denote the

initial state, during the first pulse with $i = +$ or $i = -$, similarly the final state of the molecule at the second pulse is $f = +$ or $-$. Since the random phase $\Delta\theta = \omega_0 \Delta + \nu(T^+ - T^-)$ where $T^\pm$ are occupation times in states $+$ and $-$ [13], satisfying $\Delta = T^+ + T^-$, the joint PDF $P(i, f, \Delta\theta)$ is equivalent to the joint PDF $h(i, f, T^+)$ of finding the molecule in state i in the first pulse, state f in the second and with the occupation time T^+ between the two pulses. We leave technical details on the calculation of $h(i, f, T^+)$ for a longer publication, taking averages over Eq. (5) gives:

$$\langle P_n \rangle = \sum_{i=\pm, f=\pm} \mathcal{P}^{if} P_n^{\text{Cla}} [\omega(i), \omega(f)] + e^{-\Gamma\Delta/2} \left\{ e^{i(\omega_0 - \nu)\Delta} \hat{h}(i, f, -2i\nu) A_n^{\text{Coh}} [\omega(i), \omega(f)] + \text{C.C.} \right\}, \tag{10}$$

where $\hat{h}(i, f, -2i\nu)$ is the Laplace $T^+ \to 2i\nu$ transform of $h(i, f, T^+)$

$$\hat{h}(\mp, \pm, -2i\nu) = e^{-\Delta(R-i\nu)} \frac{\sinh\left[\Delta\sqrt{R^2 - \nu^2}\right] R}{2\sqrt{R^2 - \nu^2}}, \quad \hat{h}(\pm, \pm, -2i\nu) = \frac{e^{-\Delta(R-i\nu)}}{2} \left[\cosh\left(\Delta\sqrt{R^2 - \nu^2}\right) \pm \frac{i\nu \sinh\left(\Delta\sqrt{R^2 - \nu^2}\right)}{\sqrt{R^2 - \nu^2}} \right] \tag{11}$$

while $\mathcal{P}^{\pm\pm} = [1 + \exp(-2R\Delta)]/4$, $\mathcal{P}^{\pm\mp} = [1 - \exp(-2R\Delta)]/4$, are probabilities of finding the particle initially in state i and finally in state f, which are easy to obtain from Poissonian statistics.

As an illustration we apply Eq. (10) to the case of two infinitely strong $\Omega T = \pi$ pulses, so no coherence is built. At first assume that $\Omega \ll \nu$ and $\omega_L = \omega_0 + \nu$ so that the laser is in resonance with the $+$ state and not with the $-$ state. With this selective limit unlike the impulsive limit, temporal resolution is found

$$\langle P_0 \rangle = \frac{1}{4} \left(1 + e^{-2R\Delta}\right)\left(1 + e^{-\Gamma\Delta}\right), \quad \langle P_1 \rangle = \frac{1}{2}\left(1 - e^{-2R\Delta}\right) \tag{12}$$

and $\langle P_2 \rangle = 1 - \langle P_0 \rangle - \langle P_1 \rangle$. These results make perfect physical sense, because the molecule emits a single photon only when it is once in state $+$ and once in state $-$, hence $\langle P_1 \rangle = \mathcal{P}^{+-} + \mathcal{P}^{-+}$. These simple solutions show that for weak fields $\Omega \ll \nu$ the photon statistics does not depend on frequency shifts ν, and hence to explore the dynamics of the molecule we must consider stronger fields. Using Eq. (10) for π pulses, we find the exact expression

$$\langle P_1^{\text{Cla}} \rangle = \frac{4\nu^2 + \Omega^2 \cos^2\left[\sqrt{1 + \left(\frac{2\nu}{\Omega}\right)^2} \frac{\pi}{2}\right]}{4\nu^2 + \Omega^2} \tag{13}$$

$$\left\{ \frac{1 - e^{-2R\Delta}}{2} + \frac{1 + e^{-2R\Delta}}{2} \frac{\Omega^2}{\Omega^2 + 4\nu^2} \sin^2\left[\sqrt{1 + \left(\frac{2\nu}{\Omega}\right)^2} \frac{\pi}{2}\right] \right\}$$

which reduces to Eq. (12) in the limit $\Omega \ll \nu$. In the opposite limit $\Omega \gg \nu$ we have $\langle P_1 \rangle = 0$. Hence for the investigation of spectral shifts and rates we cannot use neither too weak or too strong fields which with the condition $\Omega T = \pi$ means that pulses must not be chosen arbitrarily short. Eq. (13) shows precisely what fields yield information on the process beyond simple limits.

Fast modulation.– An interesting case is the fast modulation limit $R \gg \nu$, where motional narrowing effects take place. We consider the limit $R \to \infty$ and $\nu \to \infty$, in such a way the the spectral diffusion dephasing rate $\Gamma_{\text{SD}} = \nu^2/R$ is finite. The latter is a measurable physical observable since it gives the width of the line shape in continuous wave spectroscopy [12]. To obtain the photon statistics in this limit we can proceed by expanding the exact solution Eq. (10) in terms of the large parameters R and ν. However, there is a more general and simpler approach. Notice that $\nu \ll R \ll 1/T$ and to have a finite probability of photon emission ΩT must remain a constant of order unity, therefore $\nu \ll \Omega$. Hence in this fast modulation limit the pulses must be impulsive. Then Eq. (7) holds with $\phi(\Delta) = \exp(-\Gamma_{\text{SD}}\Delta/2)$, which means that $(\Gamma_{\text{SD}} + \Gamma)/2$ is the renormalized decay rate which damps the coherence terms. This result is valid for many types of fast spectral diffusion processes, and is not limited to the exactly solvable two state process.

Semi-classical selective limit.– Neglecting the coherence terms and taking a laser in resonance with the $+$ state and out of resonance with the $-$ state i.e. $\omega_L =$

$\omega_0 + \nu$, $\Omega \ll \nu$ we find from the exact result Eq. (10)

$$\langle P_0 \rangle = \cos^2\left(\frac{\Omega T}{2}\right) + \sin^4\left(\frac{\Omega T}{2}\right)\left(1 + e^{-\Gamma\Delta}\right)\frac{1 + e^{-2R\Delta}}{4},$$

$$\langle P_1 \rangle = \sin^2\left(\frac{\Omega T}{2}\right) - \sin^4\left(\frac{\Omega T}{2}\right)\frac{1 + e^{-2R\Delta}}{2} \qquad (14)$$

and $\langle P_2 \rangle = 1 - \langle P_1 \rangle - \langle P_0 \rangle$. Note that these results exhibit Rabi oscillations and that $\langle P_1 \rangle$ is independent of $\exp(-\Gamma\Delta)$ the latter behavior is general: for any spectral diffusing process $\langle P_1^{\mathrm{Cla}} \rangle$ is independent of $\exp(-\Gamma\Delta)$ in the limit of short and strong pulses due to the mentioned symmetries of the matrix elements of the pulse Green function.

Summarizing perspectives.– Theoretical investigation of the new field of single molecule non-linear spectroscopy was presented. We showed that in the limit of impulsive pulses information on the photon statistics is given by the Kubo-Anderson correlation function, for any stationary spectral diffusion process. To obtain information on spectral shifts and spectral rates beyond the trivial limits, one must choose carefully the duration of pulse and its strength, as our analytical solutions clearly demonstrated. Our results can be checked in experiments in low temperature glasses, and our methods provide the theoretical basis for the investigation of fast dynamics on the single molecule level, thus opening the door for a vast number of applications.

[1] S. Mukamel *Principles of Nonlinear Optical Spectroscopy* Oxford Univ. Press. Oxford (1995).
[2] Erik M.H.P van Dijk et al *Phys. Rev. Lett.* **94** 078302 (2005).
[3] E. Barkai, Y.J. Jung, and R. Silbey, *Phys. Rev. Lett.* **87**, 207403 (2001).
[4] H. Yang, X.S. Xie *J. of Chem. Phys.* **117** 10965 (2002).
[5] Y. Zheng, F. L. H. Brown *Phys. Rev. Lett.* **90** 238305 (2003).
[6] S. Mukamel *Phys. Rev. A* **68** 063821 (2003).
[7] E. Barkai, Y. Jung and R. Silbey *Annual Review of Physical Chemistry* **55**, 457 (2004).
[8] I. Gopich, A. Szabo *J. of Chemical Physics* **122** 014707 (2005).
[9] E. Geva, J.L. Skinner *J. of Phys. Chem. B* **101** 8920 (1997).
[10] Y. He, E. Barkai *Phys. Rev. Lett.* **93** 068302 (2004).
[11] F. Sanda, S. Mukamel *Phys. Rev A* **71** 033807 (2005).
[12] R. Kubo, M. Toda, and N. Hashitsume *Statistical Physics 2* Springer Berlin (1995).
[13] A.M. Berezhkovskii, A. Szabo, G.H Weiss *J. of Chem. Phys* **110** 9145 (1999)
[14] In a future publication we will discuss the influence of the laser phase on the photon statistics, briefly this yields phase shifts in the coherence terms.